PB82-143405

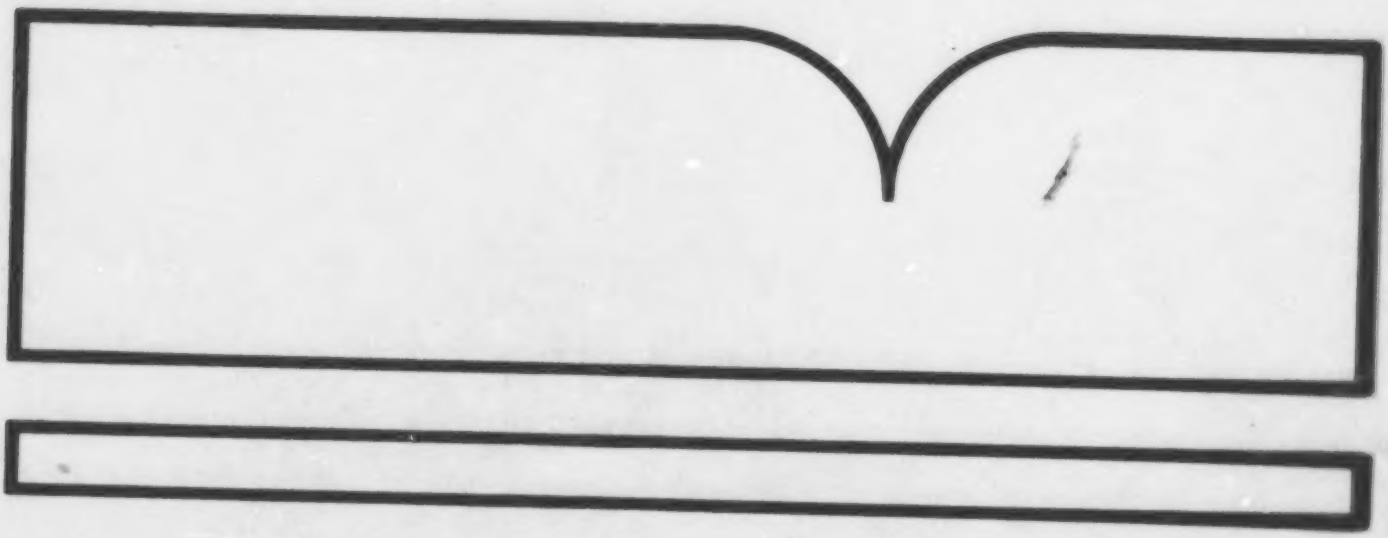
Trace Analysis for Aromatic Hydrocarbons in Natural Waters

Rockwell International
Newbury Park, CA

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

15 Jan 81



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National Technical Information Service
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TECHNICAL REPORT DATA

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1. REPORT NO	2.	3
EPA-600/J-80-365	Journal Article	PB82-143405

4. TITLE AND SUBTITLE
Trace Analysis for Aromatic Hydrocarbons in Natural Waters

5. REPORT DATE
December 1981

6. PERFORMING ORGANIZATION CODE
2362011

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Rockwell International
Environmental Monitoring & Services Center
2421 West Hillcrest Drive
Newbury Park, California 91320

10. PROGRAM ELEMENT
1NE623

11. CONTRACT/GRANT NO.
68-03-2648

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Journal Article

14. SPONSORING AGENCY CODE
EPA/600/14

15. SUPPLEMENTARY NOTES
John S. Farlow, Project Officer (201-321-6631)

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Oils Water Pollution Water Treatment Chemical Methods	Chemical Analytical Methods Aromatic Hydrocarbons Fresh Water Salt Water Brine	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	UNCLASSIFIED	
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
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SPRINGFIELD, VA 22161

Environment International, Vol. 4, pp. 407–416, 1980
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0160-4120/80/110407-10$02.00/0

EPA-600/J-80-365
Journal Article

TRACE ANALYSIS FOR AROMATIC HYDROCARBONS IN NATURAL WATERS

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(Received 18 October 1980; Accepted 15 January 1981)

A method for trace analysis of volatile aromatic hydrocarbons in natural water is described. The method is based on sparging water samples with nitrogen, adsorption of hydrocarbons on activated charcoal, followed by desorption into carbon disulfide and gas chromatographic analysis. The sensitivity of the method reaches into the 0.1 to 0.2 μg/L concentration range for individual aromatic hydrocarbons. The accuracy and reliability of the method was validated. The method was used in three field studies: dispersion of aromatic hydrocarbons discharged from the Trans-Alaska Pipeline southern terminal throughout Port Valdez; survey of the Atigun River Watershed after oil spill on June 10, 1979; and chemical characterization of treated effluents from offshore oil extraction platforms in the Gulf of Mexico.

Recent research in the treatment of oily wastewaters disclosed that a substantial amount of aromatic hydrocarbons can be discharged in treated ballast water (Lysyj *et al.*, 1979) and treated produced water (Lysyj *et al.*, 1981) from offshore oil extraction operations. It was found, for example, that benzene, toluene, and xylenes/ethylbenzene alone constitute as much as 45%–50% of all organic matter present in treated ballast water (Lysyj *et al.*, 1979). Under consent decree (Keith and Telliard, 1979), the U.S. Environmental Protection Agency (EPA) has designated benzene, toluene, and ethylbenzene as priority pollutants and the State of Alaska has established regulations for control of aromatic hydrocarbons in receiving waters. In waters designated for propagation of fish and other wildlife, the State of Alaska established a 10 μg/L limit for aromatic hydrocarbons (State of Alaska, 1979). The implementation of such a regulation requires accurate and reliable means for measuring the concentration of selected aromatic hydrocarbons at concentrations around and below 1 μg/L (1 ppb). In order to satisfy this need, the sensitivity of a procedure for determination of aromatic hydrocarbons (Lysyj *et al.*, 1980) was extended into the low μg/L concentration range and the reliability and accuracy of the method at such low concentrations was documented.

Procedures

Sampling

Depth samplers (Model XRB-135 manufactured by Hydro Products of San Diego) are used for sample collection. The sampler is a cylinder with open ends that

can be closed by snap covers triggered by release of a messenger. Two samplers located an appropriate distance from each other are used during field sampling operations. A winch equipped with a steel cable is used for lowering and retrieval of the sampling devices. The cable is measured and each 5-m segment is appropriately marked.

Analysis

An 850 to 1000 mL water sample is sparged for one-half hour with nitrogen gas at a rate of 500 mL/min and volatile organic compounds are adsorbed into standard (150 mg) activated carbon tubes obtainable from Supelco, Bellefonte, PA or Mine Safety Appliances (MSA), Pittsburgh, PA. The sparging and collection apparatus consists of glass vessels (1 to 2 L in volume) equipped with glass, Teflon, or rubber stopper. A gas dispersion tube of medium-porosity fritted glass and an adsorption train are inserted (gas-tight) into the stopper. The adsorption train consists of

(a) A drying tube—a 13-cm×6-mm i.d. glass tubing filled with 10/20 mesh Drierite with glass wool plugs at both ends;
(b) An activated charcoal tube (MSA, 150-mg size) connected to the drying tube either with a short rubber tubing or a Swagelok glass-to-glass fitting.

A 1.5 L, wide-mouth glass jar equipped with a sparging head and adsorption assembly, as shown in Fig. 1, was used in this study.

After completion of sparging, the activated carbon cartridge is opened and its contents (front and back) are transferred into two reaction vessels (2-mL volume) equipped with Mininert valve seals (obtainable from Supelco, Bellefonte, PA). One milliliter of carbon disulfide is introduced by means of a hypodermic syringe through a septum into the reaction vessels. This mode of introduction of solvent prevents loss of volatile compounds due to heat of adsorption.

Both front and back segments of the adsorption cartridge are analyzed for aromatic hydrocarbons. The absence of aromatic hydrocarbons in the back portion assures complete adsorption and retention of hydrocarbons in the front portion. Analysis of the back portion of the adsorption cartridge also indicates the value of the procedural blank.

One microliter of solvent is withdrawn by a microsyringe from the reaction vessel and introduced into the gas chromatograph (Fig. 2). Any gas chromatograph equipment with a hydrogen flame ionization detector and a column capable of resolution of benzene, toluene, and xylenes/ethylbenzene can be used for analysis of volatile aromatic hydrocarbons. In this study, a Gow-Mac gas chromatograph equipped with a hydrogen flame ionization detector and a column of 3.66 m length by 0.32 cm o.d., packed with 5% OV-17 (methylphenol silicone) on Chromosorb W-HP, 100/120 mesh, was used. The column temperature was maintained at 80 °C. Nitrogen was used as the carrier gas at a 20 cc/min flowrate.

A sensitivity of 8×10^{-12} was used for analysis of benzene, and a sensitivity of 4×10^{-12} was used for determining toluene, *m*-, *o*-, and *p*-xylenes, and ethylbenzene.

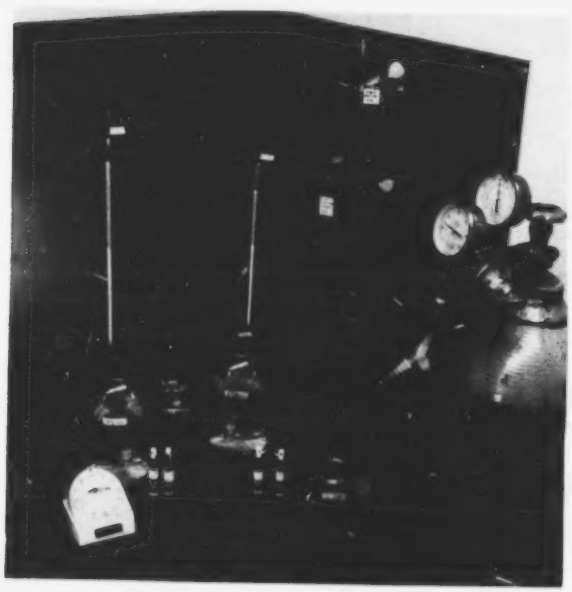

Fig. 1. Sparging and collection apparatus.

Fig. 2. Desorption vessel.

Table 1. Calibration data.

Compound	Standard solution mg/L	Equivalent to μg/L (ppb) In 850-mL sample	Response in mm Normalized at sensitivity 4×10^{-12} 9/18/79	Avg.	9/19/79	Avg.
Benzene*	1.8	2.1	98, 100, 101	(100)		
	3.5	4.1	208, 212, 216	(212)	244, 236	(240)
	14.0	16.4	752, 720	(736)	726, 726	(726)
	35.0	41.0	1952, 1952	(1952)		
Toluene	1.8	2.1	61, 62, 60	(61)		
	3.5	4.1	126, 126, 128	(127)	138, 136	(137)
	14.0	16.4	464, 448	(456)	468, 468	(468)
	35.0	41.0	1264, 1248	(1256)		
m-xylene	1.7	2.0	35, 35, 34	(35)		
	3.4	4.0	70, 69, 71	(70)	74, 74	(74)
	13.8	16.0	258, 254	(256)	262, 260	(261)
	34.4	40.0	688, 672	(680)		
o-xylene	1.8	2.1	28, 27, 26	(27)		
	3.5	4.1	58, 57, 57	(57)	60, 60	(60)
	14.0	16.4	236, 232	(234)	216, 216	(216)
	35.0	41.0	568, 560	(564)		

*Compensated for solvent blank.

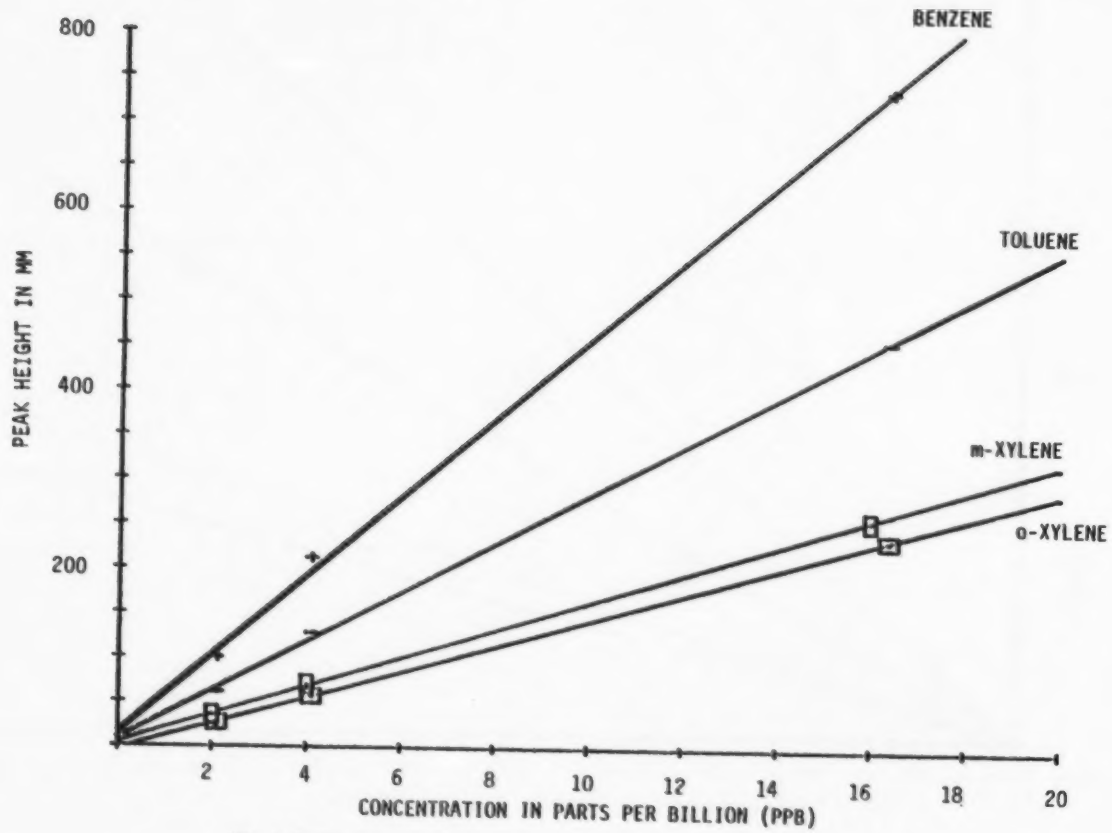

Fig. 3. Calibration curve for aromatic hydrocarbons: Low concentration range.

Experimental

The accuracy and reliability of this procedure was validated by performing the following operations.

Calibration

Four-point calibration for benzene, toluene, *m*- and *o*-xylenes was carried out. Each analysis was performed in duplicate or triplicate, and the calibration covered a 2 to 41 ppb concentration range for each of the specified aromatic hydrocarbons. All calculations reported here are based on an 850-mL water sample, the organic matter of which was concentrated into 1 mL of carbon disulfide, providing an 850-fold increase in concentration.

The calibration data is tabulated in Table 1 and displayed graphically in Fig. 3 (the low concentration range) and Fig. 4 (expanded scale). The reported data reveals that response of the gas chromatograph in the 2 to 40 ppb concentration region is linear, and the procedure is reproducible to $\pm 5\%$. For this reason, one- or two-point calibration appears to be sufficient for accurate determination.

Lower Limit of Detection

The lower limit of detection is normally defined as a signal twice the baseline noise or otherwise measurable quantity. The instrumental noise of the Gow-Mac gas chromatograph, when operated at sensitivities of 8×10^{-12} and 4×10^{-12}, is insignificant (see chromatograms in Fig. 5), and for this reason the measurable peak height of 2 mm was defined as the least detectable quantity. The mean values (duplicate or triplicate) for peak height that are proportional to concentrations of 1 μg/L of benzene, toluene, *m*- and *o*-xylene are shown in Table 2. Examination of this table indicates that the range of responses for a 1-μg/L concentration at a sensitivity of 4×10^{-12} is from 14 mm (*o*-xylene) to 49 mm (benzene). Assuming the detectable limit has a peak height of 2 mm, this would correspond to a detection limit range of 0.04 to 0.14 ppb for individual aromatic hydrocarbons.

Reproducibility (Precision)

Reproducibility data for six analyses (duplicate or triplicate determinations per analysis) are reported in Table 2. The reported data indicates that the precision

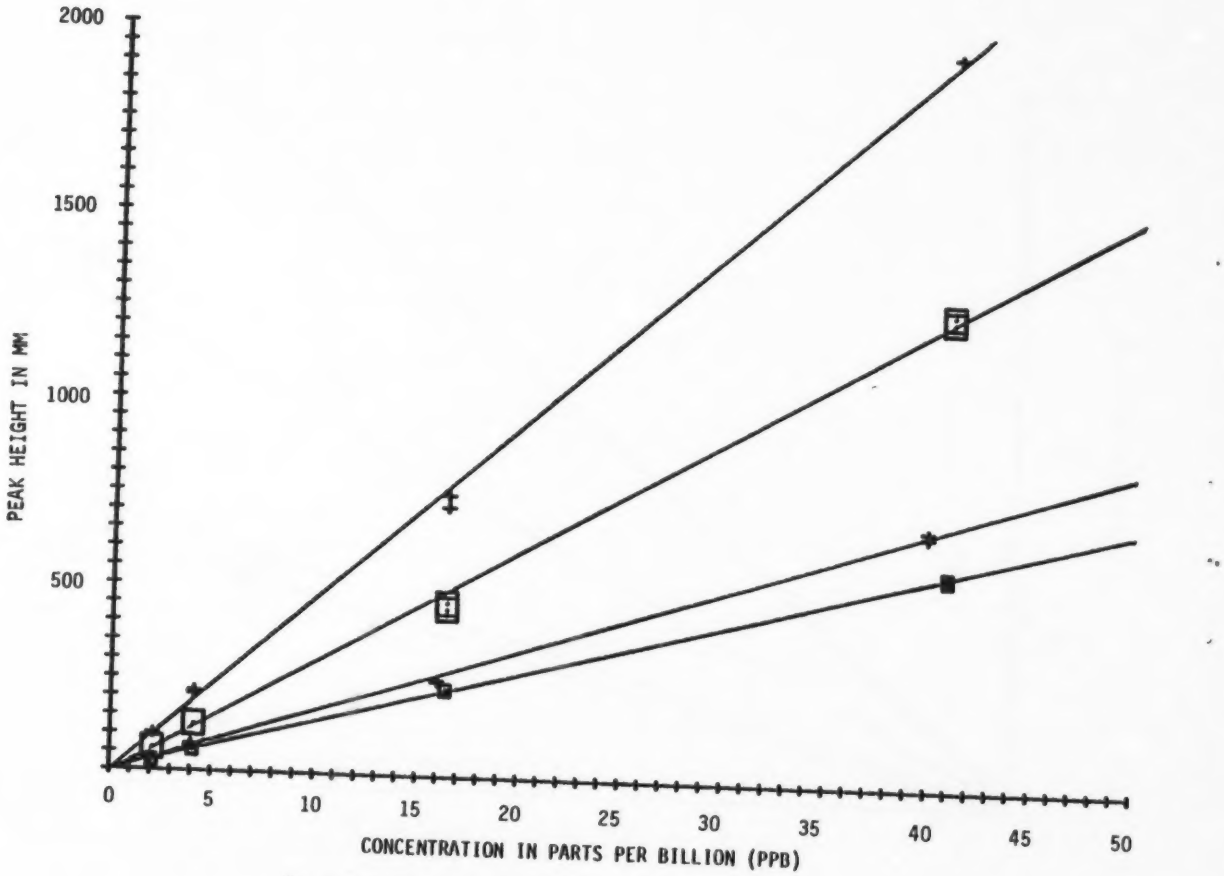

Fig. 4. Calibration curve for aromatic hydrocarbons: Expanded scale.

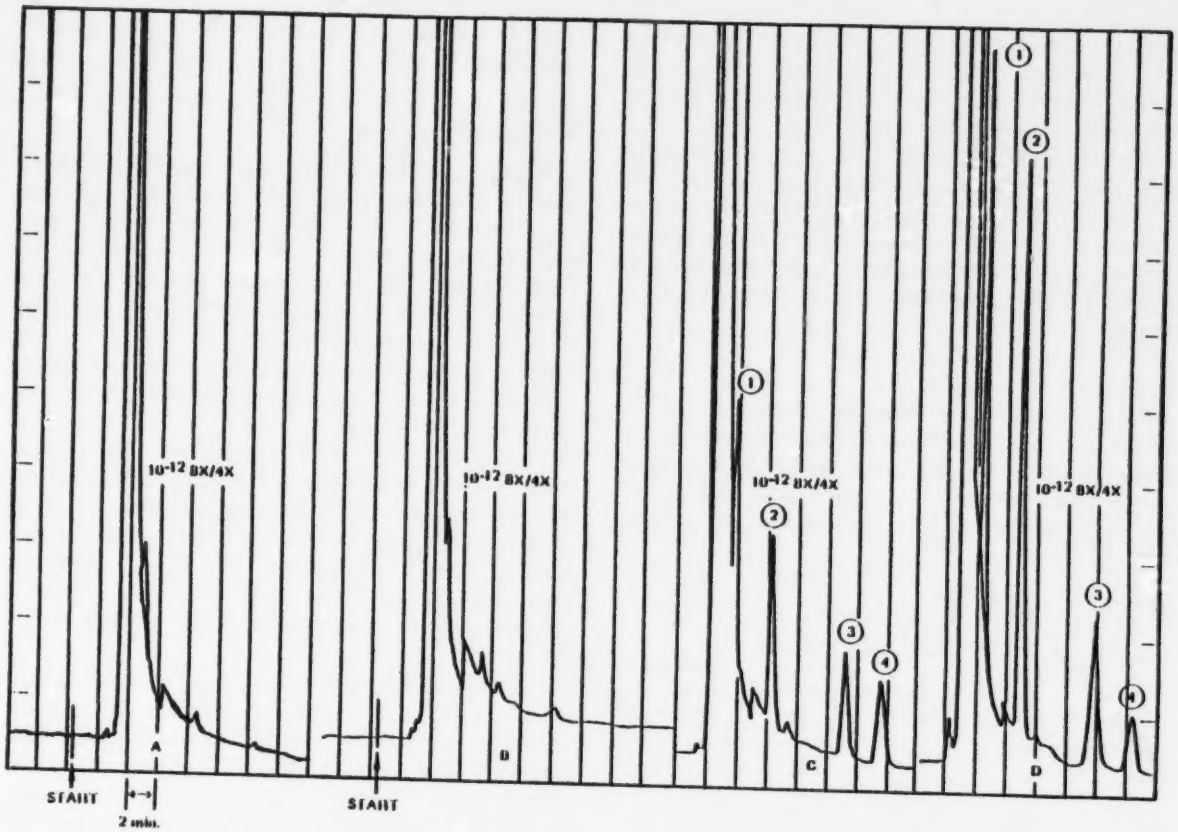

Fig. 5. Gas chromatograms of volatile hydrocarbons at ppb concentration levels. Gas chromatograms of (A) instrumental blank; (B) procedural blank; (C) standard solution 2 ppb each: (1) benzene, (2) toluene, (3) *m*-xylene, (4) *o*-xylene; (D) harbor water, boundary line diffuser zone of Port Valdez terminal facility, Station 34, depth 76 m (1 m aboveground). Determined concentrations: (1) benzene = 7.6 ppb; (2) toluene = 6.2 ppb; (3) *m*-xylene = 2.8 ppb; (4) *o*-xylene = 1.4 ppb.

of the method in the 0.5- to 40-ppb concentration range is between ±4% and ±8% for individual aromatic hydrocarbons.

Contamination Control

The trace analysis in the low-ppb concentration range required close contamination controls. Instrumental and procedural blank determinations were performed to assure the absence of false-positive contributions.

The instrumental blanks were performed daily before initiation of calibration and analysis. One milliliter of carbon disulfide was injected in the gas chromatograph and analyzed in the same manner as standard calibration solutions and unknown samples. A typical gas chromatogram of an instrumental blank is shown in Fig. 5. A small peak was usually observed for benzene. It corresponded to approximately 1 ppb of benzene and probably was due to contamination present in the solvent used. This value was compensated for in all subsequent calculations. No instrumental blank response was observed for toluene or xylenes.

Table 2. Reproducibility of results (response to 1 μg/L in mm at 4×10^{-12} sensitivity).

Compound	Peak height in mm	Average	Standard deviation
Benzene	48, 52, 45, 48, 59, 44	49	±8%
Toluene	29, 31, 29, 31, 33, 28	30	±4%
m-xylene	18, 18, 16, 17, 19, 16	17	±5%
o-xylene	13, 14, 14, 14, 15, 13	14	±4%

The procedural blank determination involved preparing synthetic seawater, which was introduced into the sampling container (used in field work) to simulate the sampling operation, and then carrying out the procedural operation in exactly the same manner as in the analysis of "real-life" samples. This analysis produced the following blank values: benzene peak height, 2 mm; toluene peak height, 7 mm; *m*-xylene peak height, 3 mm. The gas chromatograms for procedural blanks are shown in Fig. 5. In terms of concentration, they correspond to benzene, 0.04 ppb; toluene, 0.25 ppb; *m*-xylene, 0.19 ppb—or approximately 0.5 ppb of total aromatic hydrocarbons.

An additional study of procedural blanks was carried out in January, 1980. It was found that some batches of distilled water were contaminated by BTX and values as

high as 2 ppb can sometimes be expected in distilled water. It is recommended that water used for blank and recovery determinations be carefully examined for possible contamination prior to use.

The Valdez tap (drinking) water that was used in this study showed relatively low blank values: 0.3 ppb for benzene, 0.2 ppb for toluene, 0.2 ppb for *m*- and *p*-xylene, and none for *o*-xylene. Based on completed studies, it appears that procedural blank values of 0.5 to 0.7 ppb of BTX can be expected in relatively pure water samples.

Recovery

Recovery studies on benzene, toluene, *m*- and *o*-xylenes at low concentrations (2 ppb) were carried out. Results are reported in Table 3. Based on this experimental data, it appears that recoveries of 70% to 80% can be realized for BTX at the low end of the operational procedure described here, with reproducibility of approximately ±5%.

Table 3. Recovery data for benzene, toluene, *m*- and *o*-xylenes (BTX).

Compound	Sample size (mL)	Concentration (ppb)	Amount present (μg)	Amount found (μg)
Benzene	850	2.07	1.76	1.54
	850	2.07	1.76	1.85
	850	2.07	1.76	1.19
	850	2.07	1.76	1.19
	850	2.07	1.76	1.46
	850	2.07	1.76	1.48
	850	2.07	1.76	1.38
Mean and standard deviation				1.44 ± 0.23 μg
Recovery and $\delta/\sqrt{n}$				82 + 5%
Toluene	850	2.03	1.73	1.63
	850	2.03	1.73	1.72
	850	2.03	1.73	1.24
	850	2.03	1.73	1.38
	850	2.03	1.73	1.49
	850	2.03	1.73	1.43
	850	2.03	1.73	1.45
Mean and standard deviation				1.48 ± 0.16 μg
Recovery and $\delta/\sqrt{n}$				85.4 ± 3.5%
m-xylene	850	2.03	1.73	1.03
	850	2.03	1.73	1.36
	850	2.03	1.73	0.61
	850	2.03	1.73	1.09
	850	2.03	1.73	1.26
	850	2.03	1.73	0.91
	850	2.03	1.73	1.17
Mean and standard deviation				1.06 ± 0.25 μg
Recovery and $\delta/\sqrt{n}$				61.4 ± 5.4%
o-xylene	850	2.07	1.76	0.66
	850	2.07	1.76	0.93
	850	2.07	1.76	0.22
	850	2.07	1.76	0.76
	850	2.07	1.76	0.89
	850	2.07	1.76	0.50
	850	2.07	1.76	0.44
Mean and standard deviation				0.69 ± 0.25 μg
Recovery and $\delta/\sqrt{n}$				39 ± 5.4%

Applications

Volatile aromatic hydrocarbons including benzene, toluene, ethylbenzene, and xylenes are found in treated oily wastewaters discharged from various operations involving extraction, transport, and refining of petroleum. Benzene, toluene, and ethylbenzene are also designated by the U.S. Environmental Protection Agency as priority toxic pollutants (Keith and Telliard, 1979). The State of Alaska limits concentration of aromatic hydrocarbons in waters designated to propogation of fish and other wildlife to 10 μg/L.

A study dealing with the effectiveness of a large-scale treatment of oily wastewater was conducted at the terminal facility of the Trans-Alaska pipeline in Valdez, Alaska (Lysyj *et al.*, 1979) in 1978–1979 disclosed that benzene, toluene, ethylbenzene, and xylenes contribute approximately 50% to the total organic load of treated effluent and are discharged at a rate of 200 to 300 L/day.

Studies dealing with effectiveness of offshore produced (brine) water treatment on offshore oil extraction platforms in Cook Inlet, Alaska, were conducted in 1979 and 1980 (Lysyj *et al.*, 1981) and disclosed that treated effluent also contained a significant amount of volatile aromatic hydrocarbons. Average concentrations of benzene, toluene, and ethylbenzene/xylenes in the treated effluent were found to be in the 9 to 10 mg/L range. Typical composition of aromatic hydrocarbons in effluents from offshore platforms in this case was found to be 6 mg/L benzene, 3 mg/L toluene, and 1 mg/L ethylbenzene/xylenes.

In order to determine how effectively volatile aromatic hydrocarbons are dispersed by the diffuser of the treatment plant in Valdez Harbor, a study was carried out in the mixing zone of the Valdez marine terminal in 1979–1980 (Lysyj *et al.*, 1981). Horizontal and vertical transects were designed for a sampling grid around the diffusion zone. Samples of seawater were collected and analyzed for aromatic hydrocarbons. Concentrations of aromatic hydrocarbons ranging between 20 and 120 μg/L were found at the mixing zone boundary in the near-bottom environment. The level of pollutants declined rapidly in the vertical plane, indicating poor vertical mixing during periods of thermal and density stratification of the receiving water. The maximum concentration of aromatic hydrocarbons was found within 10 m of the bottom during late summer maximum stratification of receiving waters.

As demonstrated by these studies, aromatic hydrocarbons designated by the EPA as priority toxic pollutants (benzene, toluene, ethylbenzene) are discharged in significant amounts into the receiving environment. Concentrations of such compounds dissipate in ambient

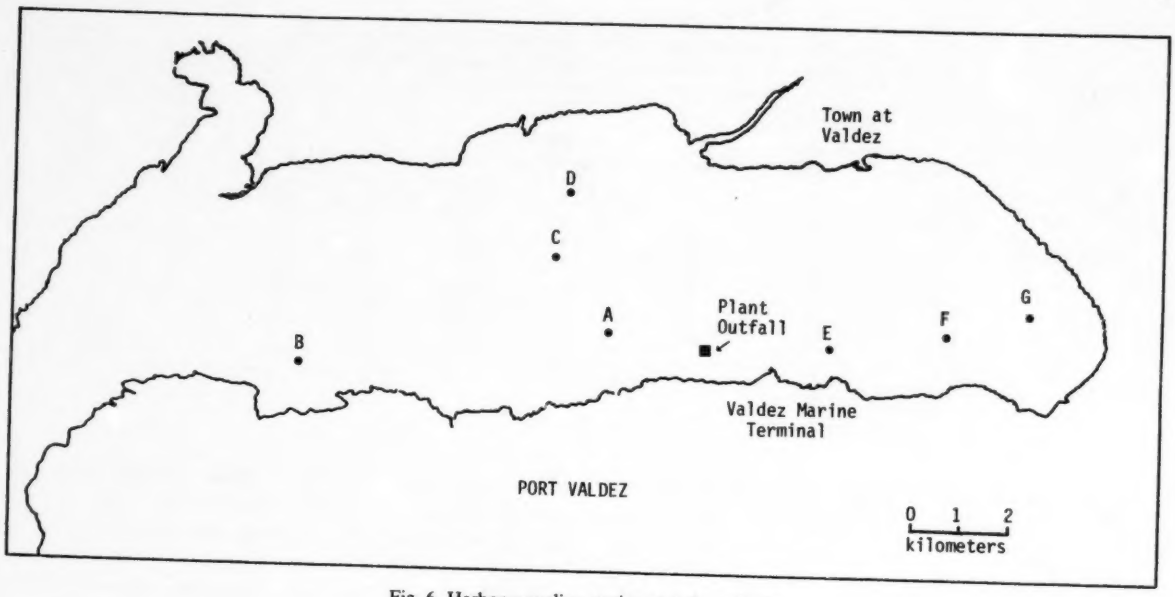

Fig. 6. Harbor sampling stations (*A* through *G*).

waters as a result of physical diffusion, chemical oxidation, and biological assimilation.

In order to study the ultimate fate and environmental impact of aromatic hydrocarbons, reliable and sensitive field procedures for measuring benzene, toluene, and ethylbenzene are needed. The method as described in this publication fulfills such a need. It was proven to be a rugged, simple, and reliable analytical procedure well suited for field operations with required high order of sensitivity. Three examples of successful field application are described below.

Fig. 7. Sampling of harbor water in Port Valdez, Alaska.

Port Valdez, Alaska

Studies conducted at Valdez Marine Terminal disclosed that very little vertical mixing occurs in the diffuser area during periods of thermal and density stratification in the harbor (Lysyj *et al.*, 1981). The effluent from the plant forms a submerged field of pollution just below the zone of stratification and disperses in a vertically thin, pancakelike configuration across the harbor. The extent of such a spread was studied using analytical techniques described in this presentation.

To study the spread of aromatic hydrocarbons into the harbor, a horizontal transect of seven sampling stations was devised at uniform depths of 60 m, which corresponded approximately to the depth at the beginning of the pronounced thermal and density stratification of the upper water column during late summer months.

The harbor sampling stations were selected as follows: Station *A*, approximately 1.5 km from the plant outfall in a generally westerly direction; Station *B*, approximately 9 km in a westerly direction; Station *C*, approximately 3.5 km in a northwesterly direction (middle of the harbor); Station *D*, approximately 5 km in a northwesterly direction; Station *E*, approximately 2.5 km in an easterly direction; Station *F*, approximately 5 km in an easterly direction; and Station *G*, approximately 6.75 km in a northeasterly direction (proposed

Table 4. Aromatic hydrocarbons in Valdez Harbor: Horizontal distribution outside the diffuser zone at 60-m depths, September 1979 study (sampling dates: September 12 and 13, 1979).

Station No.	Distance from the plant outfall (km)	Temperature (°C)	Total aromatic hydrocarbons (μg/L)	Benzene (μg/L)	Toluene (μg/L)	Xylenes (μg/L)
*A**	1.5	5.5	<0.5	ND**	ND	ND
*B**	9.0	6.0	<0.5	ND	ND	ND
*C**	3.5	5.5	1.2	0.7	0.3	0.2
*D**	5.0	5.8	<0.5	ND	ND	ND
*E**	2.5	6.0	1.2	0.3	0.2	0.7
*F**	5.0	6.0	<0.5	ND	ND	ND
*G**	6.8	–	<0.5	ND	ND	ND

*See map, Fig. 6.
**Not detected.

outfall of the planned refinery). The selected transect generally radiated along the shoreline in westerly and easterly directions, and across the harbor in a northwesterly direction. Samples were collected at each sampling station at a depth of 60 m, sampling operations from a research vessel are depicted in Fig. 7.

The samples were analyzed for aromatic hydrocarbons and results are reported in Table 4. Examination of this table indicates that aromatic hydrocarbons spread approximately 2 to 3 km in northerly and easterly directions. No hydrocarbons were found in the harbor in the westerly direction, nor at stations further down the easterly direction.

On the basis of this data, it must be concluded that a significant segment of Port Valdez is affected by aromatic hydrocarbon pollution during late summer months, when pronounced density and thermal stratification of the water body takes place.

Fig. 8. Sampling near Trans-Alaskan Pipeline at Atigun Pass.

Atigun Pass, Alaska

An oil spill occurred at Atigun Pass on 10 June 1979 when the Trans-Alaska Pipeline developed a leak due to a crack produced by geological shift of underlying strata. The spill occurred near Pipeline Milepost 166 approximately 250 km south of the Arctic Ocean at Atigun Pass on the north slope of Brooks Range (Morris, 1979). Crude oil from the leak was swept down and accumulated along the banks of the Atigun River. A broken grey sheen was observed within the first 40 km of this watershed. Vegetation on sand bars and gravel areas were contaminated. The spill containment action was undertaken at once and a team of U.S. Wildlife Service arrived on the scene to conduct biological damage assessment studies (Morris, 1979). The survey concluded that in view of the absence of fish, scarcity of invertebrates, and oil contaminated substrate conditions, there was indication of adverse impact to the aquatic resources but to an unknown extent. The possibility of toxic dissolved fraction of crude oil (benzene, toluene, xylenes) was suggested as a possible factor (Morris, 1979).

To explore this hypothesis, a water sampling program of the upper reaches of Atigun River was carried out on June 26–28, 1979. The sampling operation is depicted in Fig. 8. The containment area of the spill was approximately 40 km long by 1 km wide. Its upper reach was at the Atigun Pass, and the lower near Bridge No. 2. The aerial overflight of the containment area originated near Bridge No. 2 at the northerly terminal of the containment area, and proceeded in a southerly direction toward the origin of the oil spill at the Atigun Pass. Frequent ground stops were made over the entire length of the containment area, and visual examinations for presence of oil were made of the shoreline, water stream, and gravel bed.

Based on a visual survey of the containment area and consultation with ground teams of the U.S. Fish and Wildlife Service and the Alyeska cleanup crew, the containment area was divided into four zones, each representing different levels of oil contamination or effects. Zone 1 was in the immediate area of the spill on the northerly slope of Atigun Pass. Zone 2 covered approximately 15 km of the northerly reach of the Atigun River. Zone 3 covered 26 km downstream from Zone 2, and Zone 4 was designated as a bed of the Atigun River between Bridge No. 2 and the Arctic Ocean.

Sample collection was carried out on 28 June 1979. Helicopters, off-road vehicles, and foot transports were utilized in this operation. Sets of two to three samples of one-liter size were collected in each zone and preserved by acidification using 1 : 1 diluted hydrochloric acid.

The aromatic hydrocarbon content of collected samples was determined using a procedure described in this presentation. Results are reported in Table 5. Examination of the data indicates that trace amounts of aromatic hydrocarbons were present in the effluent from containment ponds (approximately 4 μg/L). No aromatic hydrocarbons were found in the affected watershed. On the basis of this observation, it must be concluded that 18 days after the spill, dissolved toxic fraction of crude oil was absent from the watershed of the containment area.

Table 5. Analysis for aromatic hydrocarbons in the Atigun River, Alaska.

	Concentration, μg/L			
	Total	Benzene	Toluene	Xylenes/ Ethylbenzene
Effluent from containing ponds	4.3	0.8	2.3	1.2
7 miles downstream*				
9 miles downstream*	>0.5	ND**	ND	ND
17 miles downstream*	>0.5	ND	ND	ND
25 miles downstream*	>0.5	ND	ND	ND
Tributary to Atigun River (control sample)	>0.5	ND	ND	ND

*Distance is given from containment area.
**Not detected.

Gulf of Mexico

Offshore extraction in the Gulf of Mexico is a major source of crude oil. As a result of such extraction, produced water (brine) is generated. This water is contaminated by petroleum and must be treated before it can be safely discharged into the environment. The treatment processes include gravity separation and flotation. Studies carried out in the Cook Inlet, Alaska, offshore operations disclosed that treated effluent contains significant amounts of aromatic hydrocarbons (Lysyj *et al.*, 1981).

To investigate the possible presence of such compounds in treated effluent from offshore platforms in the Gulf of Mexico, sampling was carried out on six platforms. The samples were analyzed for benzene, toluene, and xylenes/ethylbenzene using procedure described in this paper. The results are reported in Table 6. The examination of this table indicates that volatile aromatic hydrocarbons, including benzene, toluene, and xylenes/ethylbenzene, are indeed present in offshore produced water, but in lower concentrations than found in Cook Inlet, Alaska.

Table 6. Volatile aromatic hydrocarbons in treated effluents from offshore platforms in the Gulf of Mexico.

		Concentration in mg/L			
Date	Platform	Benzene	Toluene	Xylenes/ Ethylbenzene	Total
3/7/80	1	0.9	0.7	0.3	1.9
3/10/80	2	0.5	0.6	0.3	1.4
3/21/80	3	0.8	0.4	0.2	1.4
3/24/80	4	0.4	0.4	0.2	1.0
4/2/80	5	2.4	2.1	0.3	5.8
4/4/80	6	1.4	0.7	0.3	2.4
Average		1.1	0.8	0.3	2.2

Acknowledgements— This project has been funded with Federal funds from the U.S. Environmental Protection Agency under contract number 68-03-2648. The content of this publication does not necessarily reflect the views or policies of the U.S. Environmental Protection Agency, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government.

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